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# Multi-Center Electronic Structure Calculations for Plasma Equation of State

B. G. Wilson, D. D. Johnson<sup>†</sup>, A. Alam<sup>†</sup>

Lawrence Livermore National Laboratory

P.O. Box 808, Livermore, CA 94550

<sup>†</sup>Ames Laboratory, U.S. DOE (311 TASF)

Iowa State University, Ames, Iowa 50011-3020

## Abstract

We report on an approach for computing electronic structure utilizing solid-state multi-center scattering techniques, but generalized to finite temperatures to model plasmas. This approach has the advantage of handling mixtures at a fundamental level without the imposition of ad hoc continuum lowering models, and incorporates bonding and charge exchange, as well as multi-center effects in the calculation of the continuum density of states.

## 1. Introduction

The generation of plasma equation of state data over wide ranges of temperature, density and material composition<sup>1</sup> is a computationally intensive task. For this reason there is a traditional reliance on single ‘average-ion-in-jellium’ models [<sup>2, 3, 4</sup>], to produce tabulated data for pure elements, together with a model assumption for mixing components for non-heterogeneous plasmas.

There are two main computational challenges with this model. The first is the proper description of the thermodynamic contribution from the spherically symmetric effective field of infinite extent and overall charge neutrality [<sup>5</sup>]. The second is the precise description of resonance features exhibited in the continuum density of states [<sup>6, 7</sup>], as these are essential for accurate thermodynamic consistency as the material pressure ionizes [<sup>8</sup>]. The latter in principle is a straightforward but numerically demanding task, wavefunctions arising from single isotropic scattering are simple 1-dimensional functionals of the self-consistent-field potential [<sup>9</sup>].

The main objection to the model is that it is expected to be inaccurate in the warm dense matter regime, as it is well known from the cold and solid-state limit that the electronic wave-function behavior strongly reflects the influence of multiple ion centers. This influence manifests itself energetically in two inter-related behaviors. Sharply defined bound states spread into bands due to the overlap of wavefunction tails on neighboring nuclear sites, and continuum waves engage in multiple scattering, altering the structure of the continuum density of states [<sup>10</sup>], and in particular modifying the resonance features exhibited by ion-in-jellium models [<sup>11, 12</sup>]. Theoretically this is a challenging physical process to describe, as for two or more scatterers, there are an *infinite* number of possible scattering events, and *recursive* solutions are required for wave-functions (Fig1).

The effect of multicenter wavefunctions in dense plasmas has been previously investigated for dense plasma opacities by [<sup>13, 14</sup>] and X-ray Absorption Near Edge Structure [<sup>15, 16, 17</sup>]. Our objective is to incorporate multiple scattering physics into plasma equation of state models.

For equation of state applications it is required to calculate the energetics of the plasma precisely and to also be smoothly continuous even under extreme changes in temperature and density. This necessitates an all-electron approach to the self-consistent field description. Furthermore, because of the strong isotropic form of the potential near nuclear sites, multiple locally spherically symmetric coordinate systems are advantageous for numerically modeling the exponentially varying self-consistent charge density. These constraints suggest an approach to calculating electronic structure generally known as the KKR method.

## 2. KKR methods

The KKR method, which was introduced by Korringa [<sup>18, 19</sup>], and Kohn and Rostoker [<sup>20</sup>] independently more than fifty years ago, is one of the most powerful methods of calculating electronic structures of periodic solids, and has been applied successfully to metals, semiconductors and compounds [<sup>21</sup>]. The method is formulated upon multiple-scattering theory and hence is applicable not only to periodic systems but also, for example, to isolated clusters of atoms [<sup>22, 23, 24, 25</sup>]. In addition, under a coherent potential approximation, the method can be applied to substitutionally disordered alloys [<sup>26, 27, 28, 29, 30, 31</sup>] and impurities [<sup>32, 33, 34, 35</sup>].

While the energy eigenstates were determined directly in the original framework of KKR, it is nowadays more common to rather calculate the Green's function without knowing the eigenstates [<sup>36, 37, 38</sup>]. This has several advantages over the original framework. It bypasses the time consuming process of solving the eigenvalue problem. Secondly perturbations can be treated more or less exactly; e.g. we can solve impurity problems without introducing a (oft times huge) supercell. Finally a large class of observables can be directly calculated from the Green's function. In particular the imaginary part of the diagonal greens function directly gives the charge density

$$\rho(\vec{r}) = -\frac{\text{Im}}{\pi} \int_{E_b}^{E_f} dE G(\vec{r}, \vec{r}, E)$$

which is the central iterative quantity to any local density functional theory based model of electronic structure. Furthermore, because of the Herglotz properties of the Green's function, we may distort the linear integral on the real energy axis to some convenient contour in the complex energy plane (Fig[2]).

$$\rho(\mathbf{r}) = -\frac{\text{Im}}{\pi} \int dE G(\mathbf{r}, \mathbf{r}; E) \equiv -\frac{\text{Im}}{\pi} \oint dZ G(\mathbf{r}, \mathbf{r}; Z)$$

Because the Green's function at complex energies has the structure on the real axis that is Lorentzian broadened with a half-width proportional to the imaginary energy [<sup>39, 40</sup>], the replacement of the real energy integral by a contour integral in the complex energy plane allows a very efficient and accurate calculation of the charge density [<sup>41, 42, 43, 44, 45</sup>].

Explicitly, the Green's function is obtained in terms of the regular ' $Z_L(\vec{r}; E)$ ' and irregular ' $J_L(\vec{r}; E)$ ' solutions of the single-site Hamiltonian (at complex energy  $E$  and angular channel  $L=\{l, m\}$ ) through

$$G(\vec{r}_n, \vec{r}_m'; E) = \sum_{LL'} Z_L^\oplus(\vec{r}_n; E) \tau_{LL'}^{nm}(E) Z_L(\vec{r}_m'; E) - \delta_{nm} Z_L^\oplus(\vec{r}_n; E) J_L(\vec{r}_m'; E)$$

in terms of the scattering path operator  $\tau_{LL'}^{nm}(E)$  describing the conversion of an incoming electron wave at site ‘n’, with angular momentum index  $L$ , into an outgoing wave function at site ‘m’, with angular momentum  $L'$ , taking all possible scattering paths that start at site ‘n’ and end at site ‘m’ [46, 47]. For a periodic system, the scattering path operator can be solved by integrating over k-points in the Brillouin zone a matrix inversion of dimension  $N_{atom}(l_{max} + 1)^2$ , where is  $N_{atom}$  the number of atoms in the unit cell, and  $l_{max}$  is the maximum angular momentum channel considered.

Other quantities of interest, such as optical constants [48, 49], X-ray absorption [50], or electronic transport coefficients [51, 52, 53], can also be obtained from the Kubo-Greenwood formula in terms of the off-diagonal Greens’ functions [54, 55, 56, 57, 58].

Several recent excellent textbooks [59, 60, 61, 62] and reviews [63, 64, 65, 66, 67, 68] are available for those interested in a more in-depth expostulation of the KKR formalism. In addition, reviews applying the KKR method in the conceptually simplified framework of model 1 and 2 dimensional scattering systems are found in [69, 70, 71, 72, 73].

It is important to note that the KKR method is fundamentally a conventional one-electron averaged description of the electronic state using density functional theory [74, 75, 76] but generalized to handle multiple locally spherically symmetric scattering sites. As such it is still subject to the same approximations and limitations inherent to the average atom and density functional theory approximations.

For our purposes we have utilized and modified the University of Illinois materials science code ‘MECCA’ [77], a spin-polarized scalar-relativistic KKR code for treating complex disordered alloys [78]. Fully relativistic KKR source code is also available at [79].

### 3. Extensions for plasma descriptions

For solid state and materials science applications the KKR method is applied to complex polyatomic crystalline systems at zero temperature with perhaps substitutional disorders. For plasma applications we must consider systems where the ions positions are amorphous [80, 81, 82] or spatially disordered [83, 84, 85], in addition to the electrons being in excited states at a finite temperature.

There are three potential approaches to treating spatial disorder. The first is to take many instances of relatively small unit cells, with the intent that your ensemble is large enough to approximate plasma averages, with the assumption that ‘edge effects’ of the periodicity do not influence physical observables. The second is to take large unit cells with random ion positions in the unit cell, and assume that the cell size is large enough that ‘self averaging’ occurs [86]. The third is to analytically obtain a non-spherical average of multicenter effects to obtain an effective Green’s function [87, 88, 89, 90].

The initial studies reported here employed the first simple approach, as cpu requirements increase with the complexity of the unit cell. To construct our ensemble of random ion positions [91], we employed the algorithm of [92, 93] to generate random packings of equal sized [94] as well as poly disperse hard spheres [95]. A molecular dynamics based algorithm of [96, 97] was employed as well and found equally effective.

The relative effective hard sphere radii for poly-elemental plasmas were set by muffin-tin saddle point radii of neutral pseudo-atoms<sup>[98]</sup>. The muffin tin saddle point radii reflect an optimal boundary separating the spherical and non-spherical density between neighboring atoms, and are used in the MECCA code to tessellate the space of the unit cell into non-overlapping convex polyhedra centered about each nucleus (Fig [3]). Unlike a traditional Voronoi/Delaunay tessellation<sup>[99, 100, 101]</sup>, which is formed by the intersection of all planes placed midway between the nuclei, so-called ‘power’ tessellations<sup>[102]</sup> place the intersecting planes midway between the surfaces of effective hard spheres (Fig[4]). We employ the algorithm of<sup>[103]</sup> to efficiently power tessellate the three dimensional space of the unit cell. (For a review of Voronoi Tessilation of randomized ion positions see<sup>[104]</sup>.) This tessellation allows us to optimally integrate the charge density inside the Voronoi polyhedra to accurately determine the chemical potential. This integration is performed using radial spherically symmetric techniques inside an inscribed sphere (Fig[7a]), whereas the truncated pyramidal regions extending to the polyhedral surface are performed with numerical isoparametric methods<sup>[105, 106]</sup> (Fig[7b]). This technique is orders of magnitude faster<sup>[107]</sup> than comparably accurate results using shape function techniques<sup>[108, 109]</sup> (ie. spherical harmonic decompositions of 3-dimensional polyhedral unit step functions) (Fig[8]).

The thermodynamic extension to finite temperatures is easily accomplished by introducing Fermi occupation factors into the average electron per unit cell description, generalizing the band energy as

$$E_{band} = -\frac{\text{Im}}{\pi} \oint dZ (Z - E_f) G(Z) f(Z)$$

determining the free energy<sup>[110]</sup>  $F(T) = E(T) - TS(T)$  via the electronic entropy

$$S(T) = f(Z) \ln f(Z) - (1 - f(Z)) \ln(1 - f(Z))$$

To calculate the charge density at finite temperatures the deformation of the integration contour in the complex energy plane must be adjusted to consider the contributions of the Fermi factor<sup>[111, 112]</sup>,

$$f(Z) = \left(1 + e^{-\beta(Z - E_f)}\right)^{-1}$$

in particular the potential contribution from (Matsubara) poles<sup>[113]</sup> located at  $\omega_n = E_f + i\pi(2n + 1)k_B T$ . A modified contour employed by the MECCA code for low temperatures is shown in Fig[5]. With higher temperatures, alternative contour deformations may be more advantageous numerically. By decomposing the Green’s function into single-site and multi-site scattering contributions (by adding and subtracting the single site scattering “T” matrix from the scattering path “Tau” matrix)

$$\begin{aligned} G &= G_{\text{single-site}} + G_{\text{multiple-scattering}} \\ &= (ZtZ - ZJ) + Z(\tau - t)Z \end{aligned}$$

it is possible using Jordan’s Lemma of complex variable analysis to write the charge density as (see Fig[6])

$$\rho(\vec{r}) = -\frac{\text{Im}}{\pi} \oint dE f(E) G_{ss}(\vec{r}, \vec{r}; E) - \frac{\text{Im}}{\pi} \sum_n G_{ms}(\vec{r}, \vec{r}; \omega_n)$$

where only a finite number of Matsubara poles near the real energy axis contribute appreciably. At higher temperatures it is also anticipated that appreciable electron occupation will be found in channels of higher angular momentum [<sup>114</sup>], this decomposition allows their inclusion under a single site scattering approximation with little computational overhead.

#### 4. Comparisons with PURGATORIO calculations

Spin-unpolarized calculations were undertaken of ab-initio composite plasmas with the MECCA code in order to compare with results from PURGATORIO. Plasma mixtures were obtained from PURGATORIO using a simplistic ‘ideal-gas’ mixing paradigm where, given an input mixture density  $\rho_{\text{mix}}$  and temperature  $T_{\text{mix}}$ , pure element results {of nuclear charge  $Z_i$  and molecular atomic weight  $A_i$ } are combined by composition number fraction  $\{f_i\}$  at effective densities  $\rho_i^{\text{eff}}$  such that (a) all individual elements are at a common electron chemical potential, and (b) the Wigner-Seitz spheres are space filling

$$\sum_i \frac{A_i f_i}{\rho_i^{\text{eff}}} = \frac{1}{\rho_{\text{mix}}} \sum_i A_i f_i$$

( An alternative to condition (a) is that in lieu of the chemical potential the non-ideal free electron pressure at the Wigner sphere surface are at a common value. This results in an ambiguous definition of chemical potential.) By making such a comparison we test the ad-hoc continuum lowering of the ion-sphere model as well as the effects of multi-center scattering.

Our first comparison,  $\text{Al}_3\text{Ni}_2$ , was chosen for its admixture of ‘simple’ metallic Aluminum and a characteristic ‘d’-wave element Nickel, and was run at cold and 5eV electron temperatures, both at nominal solid density and six-fold compression. To isolate the purely electronic effects of multi-site scattering these runs were performed by scaling the D5<sub>19</sub> crystal structure [<sup>115</sup>, <sup>116</sup>, <sup>117</sup>] of the solid. In Fig.[9] we plot the computed density of states at solid density (4.73 g/cc) and in the cold limit. In order to exhibit both the valence bound states and continuum the density of states was plotted on a logarithmic scale, which tends to de-emphasize the multi-center scattering effects on the structure of the continuum. Nevertheless, although both models predict a strong ‘d’ state resonance, there are strong differences in the number of available states near threshold, resulting in 15% decrease in the chemical potential predicted by MECCA. Note also, that due to the differing local environments of the crystalline structure, there are site dependant atomic sphere occupations in the MECCA model, and MECCA exhibits a charge transfer from the aluminum to the nickel (an ionic bonding effect) not allowed in neutral ion-sphere models. Upon heating, both models predict that the ‘d’- wave resonance, rather than being broadened away, narrows up and is down shifted to the continuum Fig[10]. Cold compression (see Fig[11]) substantially alters the structure of the continuum density of

states and produces discernable plasma polarization shift differences in the bound valence states.

We use a second example, Aluminum Carbide at solid density and 5eV temperature, to illustrate the further effects that finite temperature non-crystalline ion order will have on electronic structure. Aluminum Carbide is an interesting case study because of the nominal presence of shallow carbon 2S states in an ion-sphere description. Fig[12] shows the effect of finite temperature electrons in a multiple-scattering description off of the cold ion crystal structure. Not surprisingly the 2S state will form a band of states as predicted by MECCA. Moreover, with thermal randomization of ion positions, random snapshots of the plasma ensemble show in Fig[13] that the gap between the 2S and the continuum density of states tends to fill in, providing a mechanism for effectively lowering the continuum in a manner unavailable to ion-sphere models. The amorphous ion positions also contribute approximately a  $1/5^{\text{th}}$  kT linewidth to the aluminum 2p bound state positions (not shown).

A third example, Boron Nitride, differs from the previous two compounds in two fundamental aspects. It has an open (low packing fraction)  $B_k$  crystal structure (otherwise known by Pearson symbol hP4) with strong anisotropic bonds (Fig[14]). Electronically it is known to be an insulator in the solid state. This is in strong contrast with ion-sphere models such as PURGATORIO, which shallow Nitrogen and Boron bound 2S states (Boron 2S indiscernible from the continuum onset on the scale of Fig[15]) and a partially filled smooth continuum density of states, in other words, a classic conductor. Gratifyingly, MECCA predicts a partially filled band of states below the onset of the continuum, with a deficit of available continuum states until 0.228 Hartrees into the continuum, giving an insulating gap of 9.9eV.

If one were to imagine an experiment to rapidly (and isochorically) heat Boron Nitride to an electron temperature sufficient to populate continuum states above the gap, predictions of conducting electrons (crudely defined as delocalized states above the energy zero) would still differ because of the gap by a factor of three between MECCA and PURGATORIO (3.46 versus 1.22 electrons/per site at 16eV – see Fig[16]). This discrepancy is ameliorated, however remains significant, by allowing the ion positions to thermally randomize. As seen in Fig [17], the main effect remains an effective lowering of quasi-continuous states below that predicted by ion-cell models.

The examples presented here are not intended to be the best or final prediction available by multi-center scattering models. In particular the open crystal structure of Boron Nitride would benefit from the inclusion of empty sphere atomic sites in the multi-center scattering basis, and we have not performed spin-polarized calculations in order to directly compare with the results available from PURGATORIO. Rather, these examples are intended only to be representative of multi-center effects not available from conventionally used models.

## 5. Future Directions

Further explorations concerning the quantitative convergence of thermodynamic properties of plasmas with increasing unit cell size and or ensemble sampling are clearly called for at this juncture. Clearly such studies are contingent on computational efficiency



[<sup>118</sup>], and it should be noted that each energy point along the complex energy plane integration is an independent calculation that can be computed on parallel processors.

Several computational improvements to the MECCA model can be pursued. Inconsistency between the Fermi Level and the charge density due to the KKR truncation of angular momentum channels can be compensated by Lloyd's formula [<sup>119, 120, 121</sup>], and the radial mesh about each site could be optimized to reduce interpolation error for quadrature based integration of Voronoi polyhedra.

In addition, enhanced physics modules, such as fully relativistic multi-site scattering [<sup>122, 123, 124, 125, 126, 127, 128, 129, 130, 131, 132, 133</sup>], improved exchange-correlational functionals, as well as treatments beyond the local density functional approximation [<sup>134, 135, 136</sup>], can also be incorporated. One area of active research is the extension of KKR methods to full potential / non-spherically symmetric site scatters [<sup>137, 138, 139, 140, 141, 142, 143, 144</sup>]. This approach has been hampered by the lack of an efficient calculational method for the near field corrections to the Poisson correction for charge densities of arbitrary shape [<sup>145, 146</sup>].

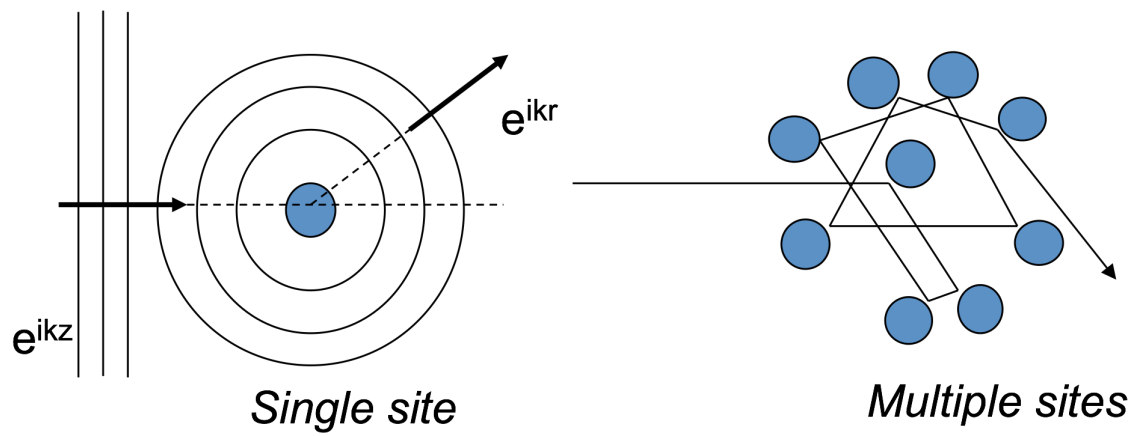
## 6. Summary

We reported on a non-spectral Green's function approach for calculating the electronic structure of spatially disordered systems at finite electron temperature. This approach has several advantages for plasma modeling. It is an all electron (no pseudo-potential) method, without ad hoc continuum lowering, that can be used for ab-initio modeling of mixtures. Comparisons with the ion-sphere model PURGATORIO showed a generic multi-site scattering effect on the density of states, namely that shallow valence bound states formed bands, with random non-crystalline order filling gaps between banded states and the positive energy continuum states to form a large effective continuum lowering.

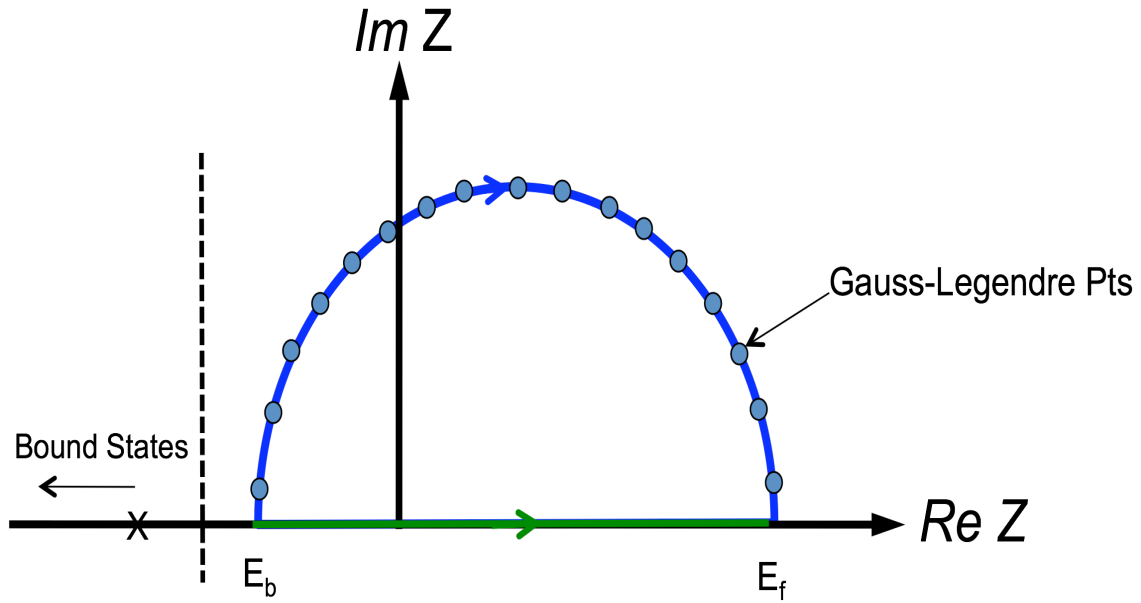
## Acknowledgments

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Fig[1]. Icon illustrating one of an infinite number of scattering path events possible with multiple scatterers.



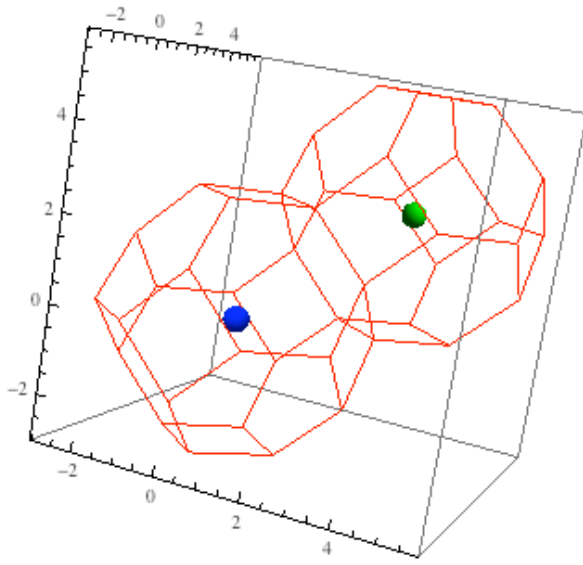
Fig[2]. Typical contour integration for zero temperature charge density. We use a Gauss-Legendre method on the parameterization of the energy in the form  $E = r e^{i\phi}$  to give

$$\int_a^b dE g(E) = \sum_n W_n f(X_n)$$

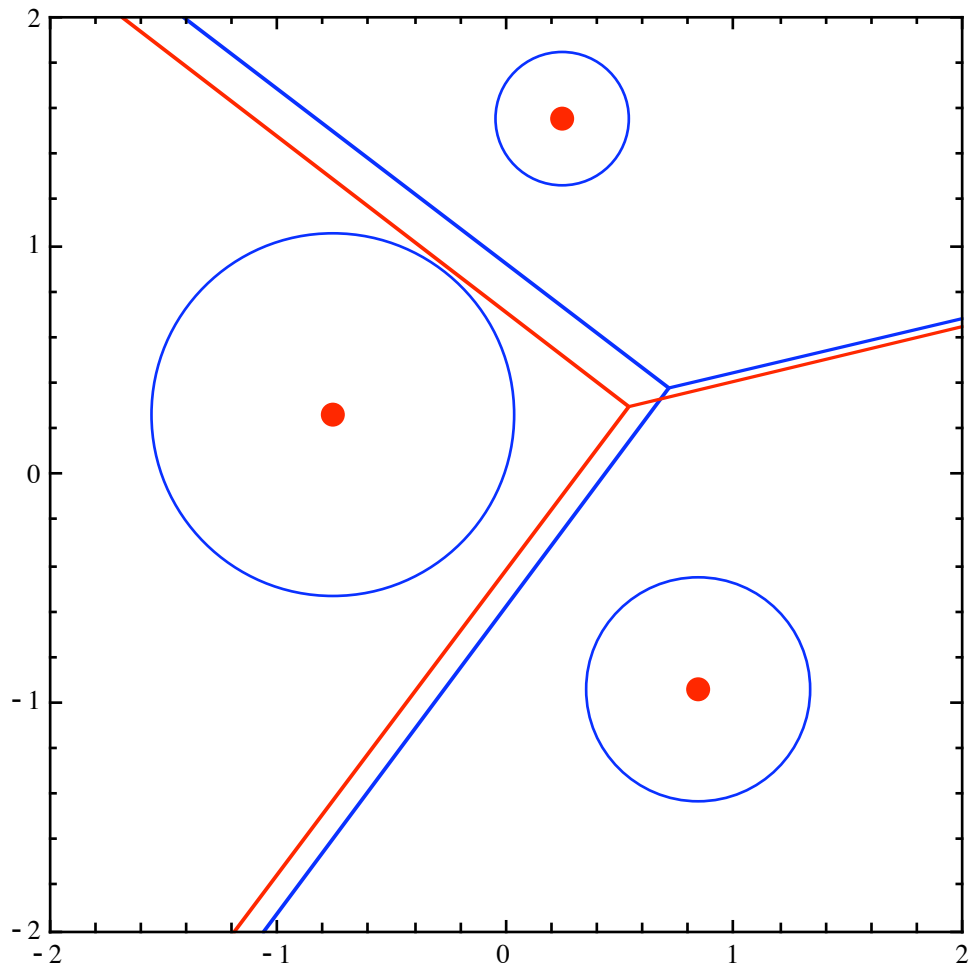
where

$$W_n = i \left( \frac{\phi_b - \phi_a}{2} \right) X_n \omega(\xi_n) \quad X_n = r \exp \left[ \left( \frac{\phi_b - \phi_a}{2} \right) \xi_n + \left( \frac{\phi_b + \phi_a}{2} \right) \right]$$

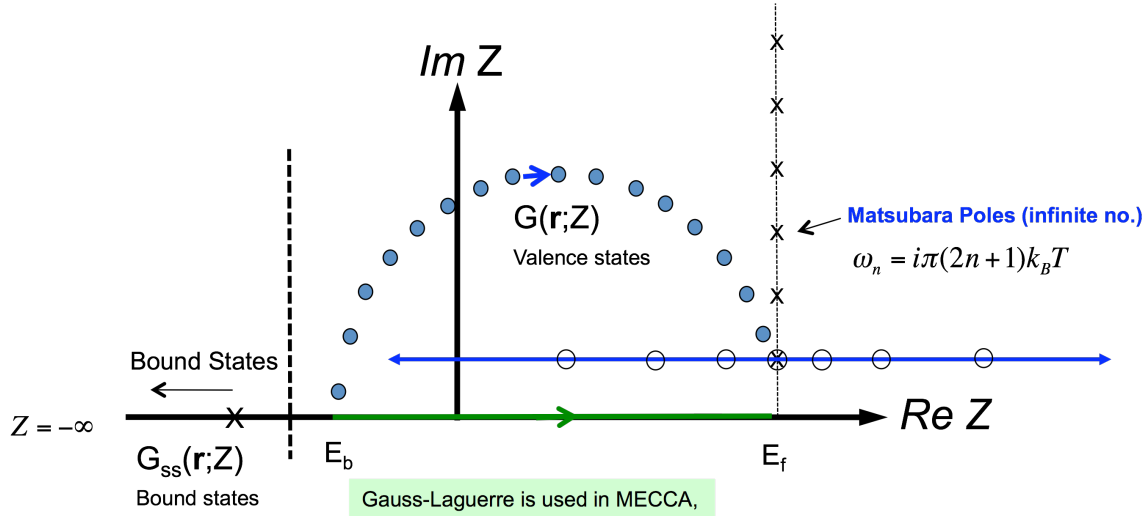
in terms of the Gauss-Legendre abscissa  $\xi_n$  and weights  $\omega(\xi_n)$ . The contribution of deeply bound core states are often approximated by their isolated atom functional form.



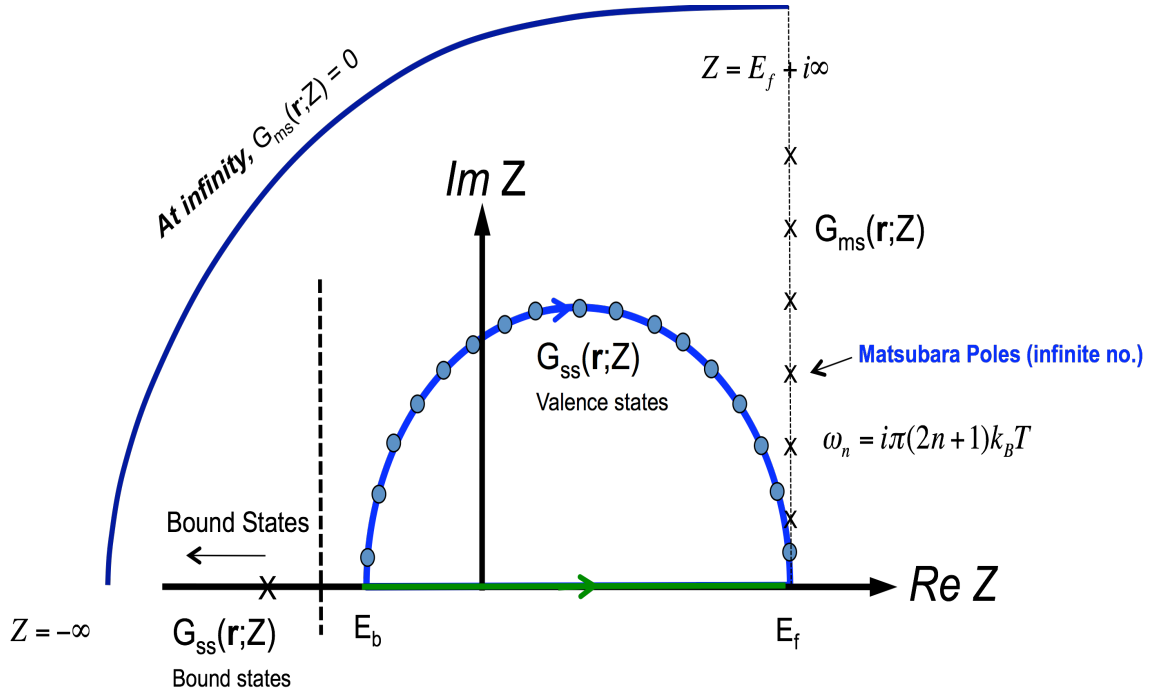
Fig[3]. Illustration of 3-dimensional Voronoi Tessellation. Shown are two polyhedra about neighboring atoms in the crystalline CsCl (B2) structure. The polyhedra are formed from 14 planes separating the nearest neighbor atoms, and results in 36 edge/24 vertex structures. Non crystalline ion positions result in complex tessellation structures.



Fig[4]. 2-d illustration of Voronoi versus power diagrams. Voronoi diagrams (red) parcel space into regions geometrically closer to one point nucleus than any other, while power diagrams (blue) parcel space into regions closest to finite effective radii of the atoms (circles).

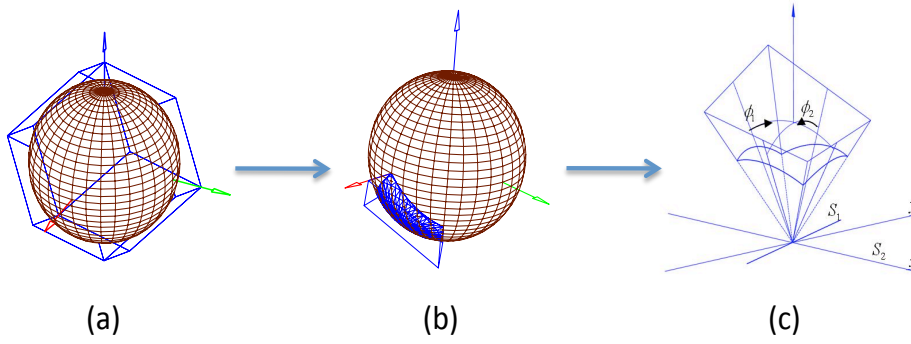


Fig[5]. Finite temperature contour integration used in MECCA code. Deeply bound core states contribute to the charge density in their isolated atom (single site scattering Green's function) form. The contribution along the semi-circular path neglects the Fermi factor, this is compensated by using a factor  $f(z)-1$  on a straight line path below the Fermi energy, and  $f(z)$  above the Fermi energy. The latter two contributions are computed using Gauss-Laguerre numerical quadrature, and they converge quickly along the path away from the Fermi energy.

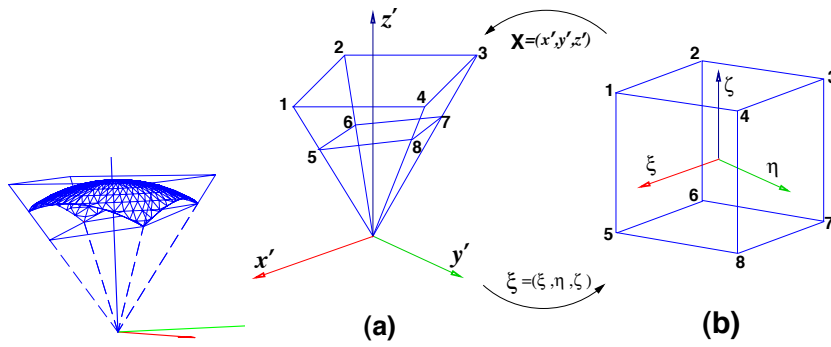


Fig[6]. Alternative complex energy contour for higher temperatures. The dimensionality of the matrices used in constructing  $G_{ms}$  are much greater than for  $G_{ss}$ , but are required for fewer discrete Matsubara frequencies as their magnitude decays with Temperature/distance from the real energy axis.

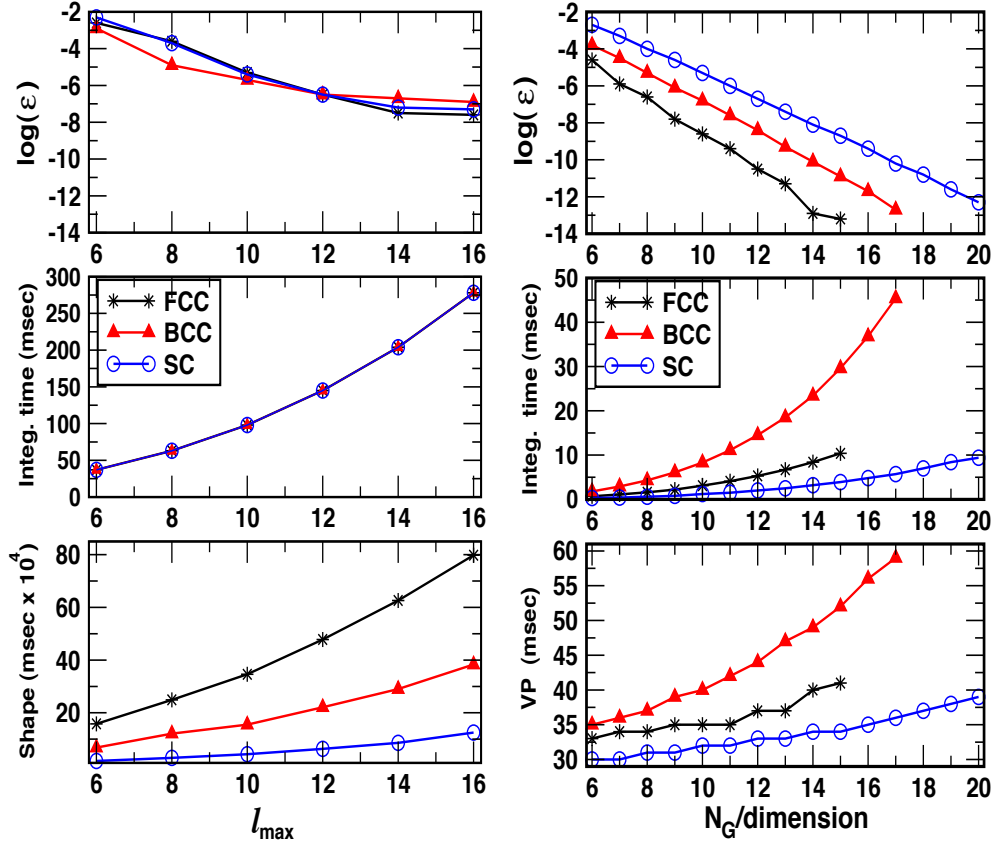




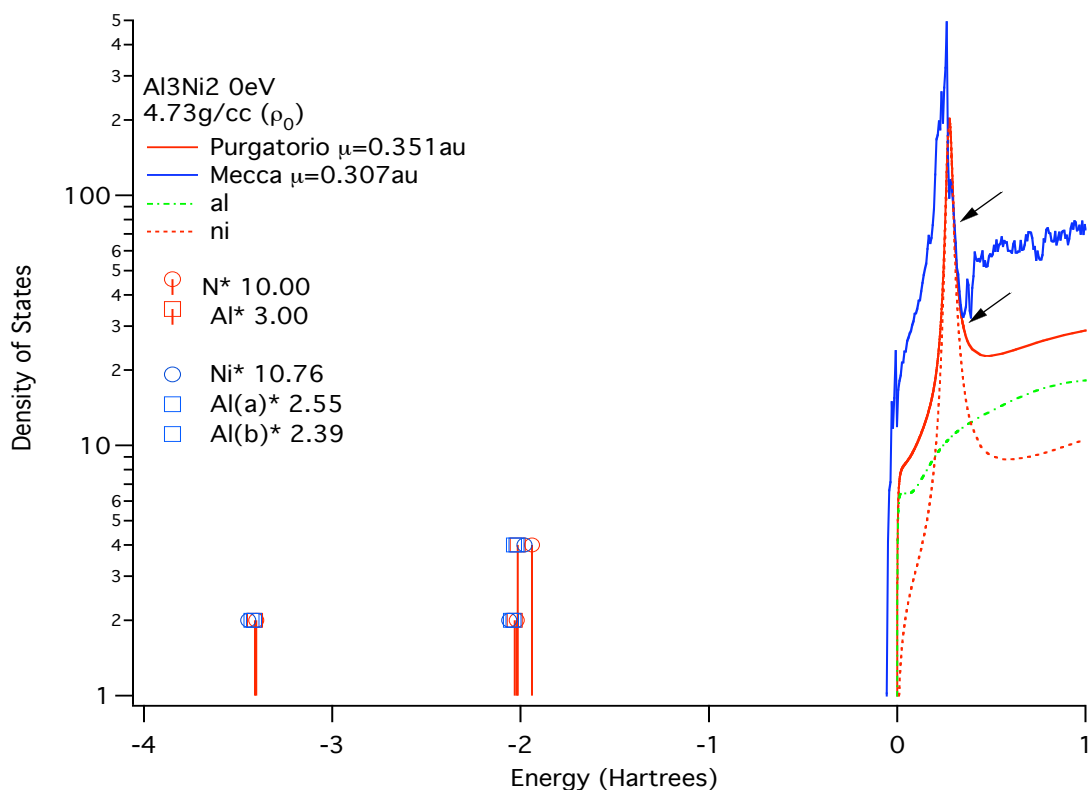
Fig[7a]. An example of a Voronoi polyhedra about a nuclear site with inscribed spherical region which can be decomposed as the union of pyramidal regions



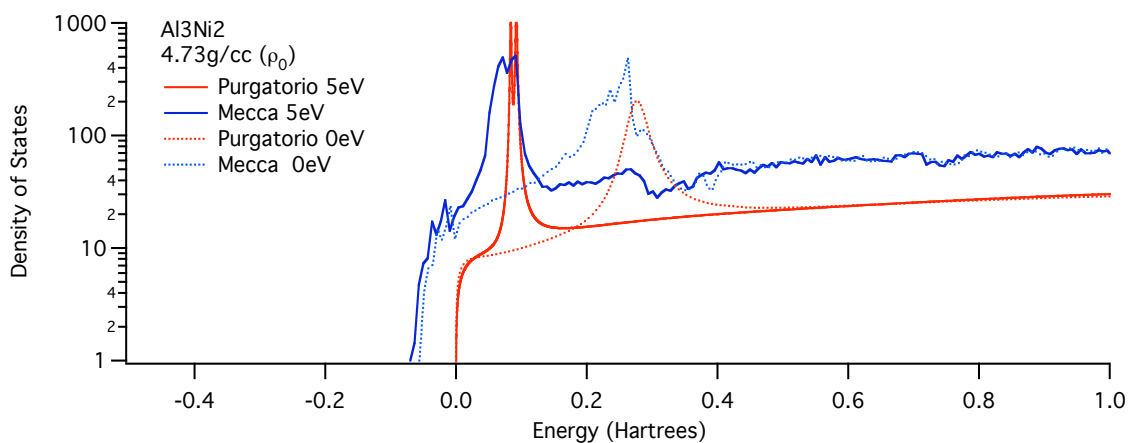
Fig[7b]. The region interior to the Voronoi surface and exterior to an inscribed sphere can be conformally mapped to a truncated pyramid, and further to a cube, for standard numerical quadrature.



Figure[8]. Comparison of time required from shape function method (left panel) vs the present method (right panel) to achieve a certain level of accuracy for an analytical Van Morgan Potential <sup>[147]</sup>. Bottom panel shows the time required for the construction of boundary information for each voronoi polyhedra, middle panel indicates the integration time and the top panel shows the logarithmic error in the interstitial charge. The three lines (with open circle, triangle and star) in each panel shows the results for SC, BCC and FCC structures respectively



Fig[9]. Density of states for crystalline ordered solid. The two in-equivalent Al sites (labeled 'a' and 'b') exhibit different average ionicities in the MECCA model due to the differing local environment, and show values differing from intuitive noble gas core values indicative of charge transfer. The arrows point to the differing prediction in the Fermi energy.



Fig[10]. The crystalline solid with electrons heated to 5eV. Both models exhibit a 'd' wave resonance state that becomes more narrowly peaked and downshifted to the continuum threshold.

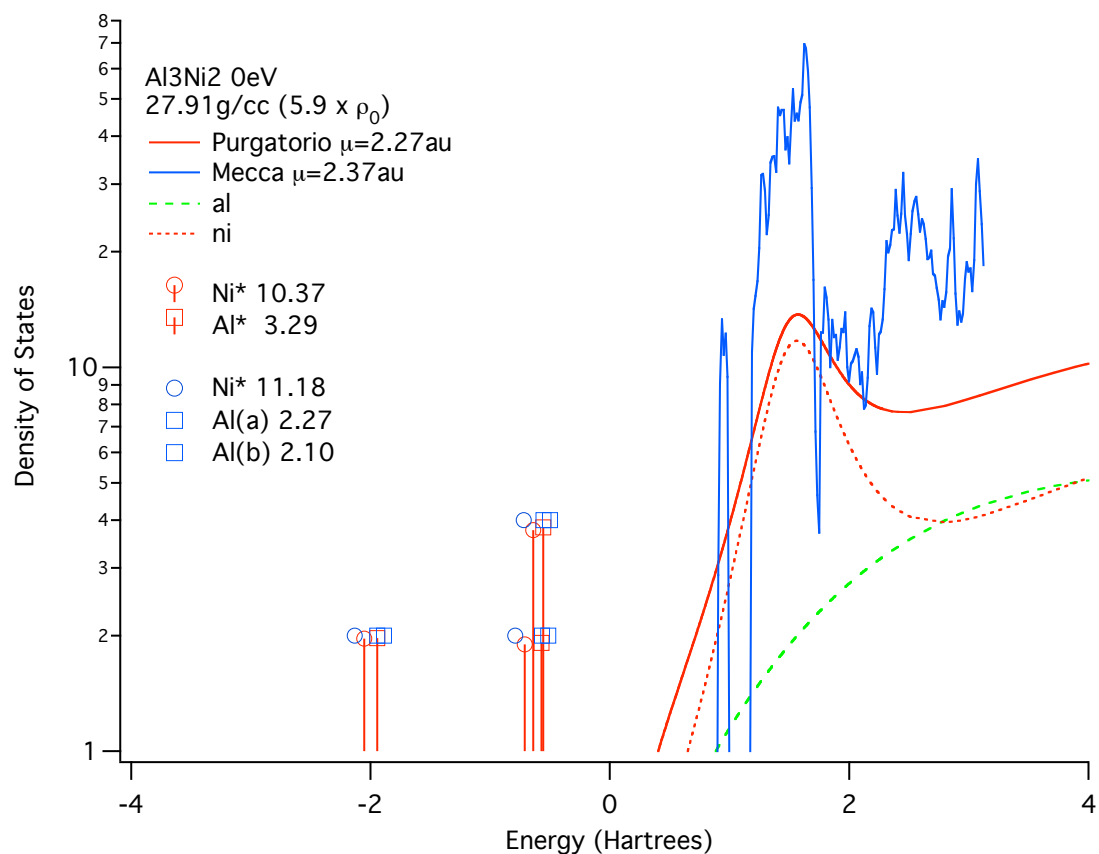
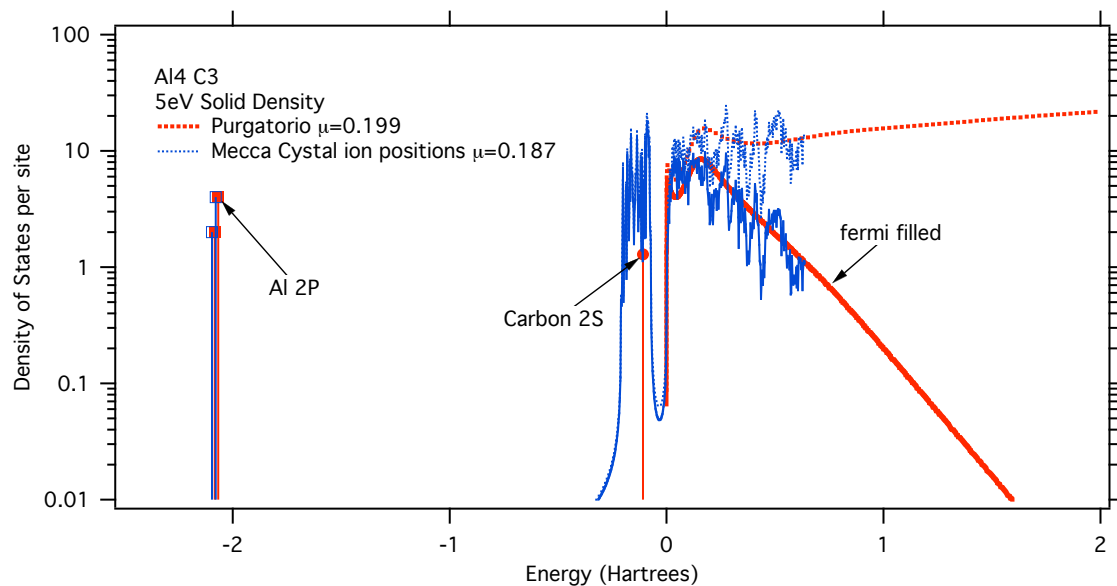
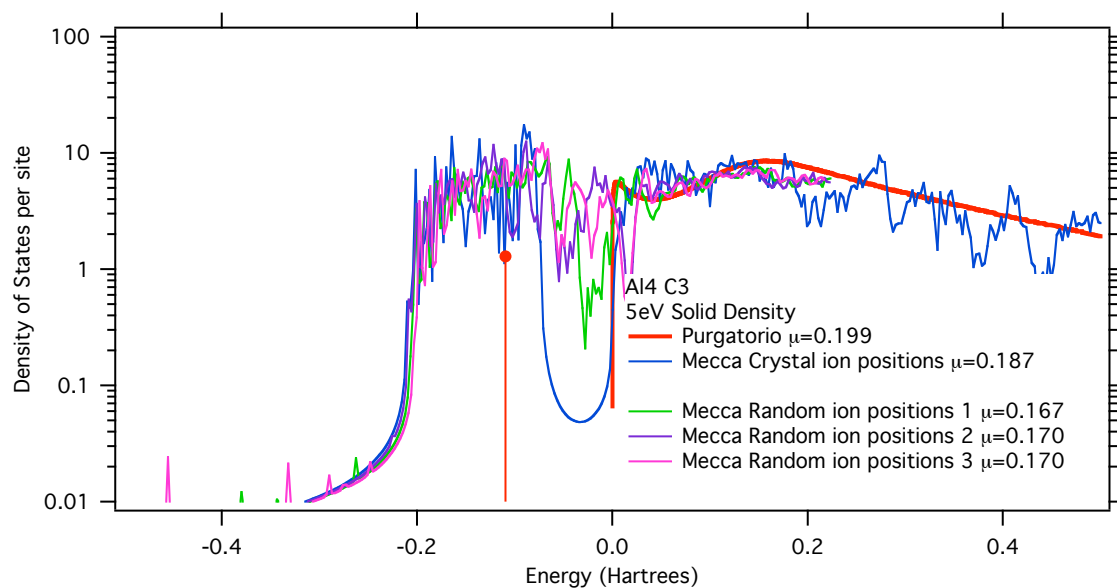


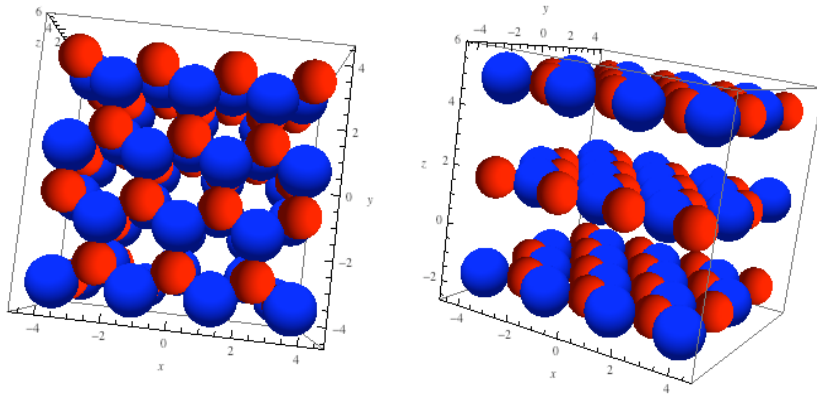
Fig.[11] Upon compression the effects of multi-center scattering on the structure of the continuum density of states become more pronounced, discernable shifts appear in the valence bound states, and charge exchange differences between models are accentuated.



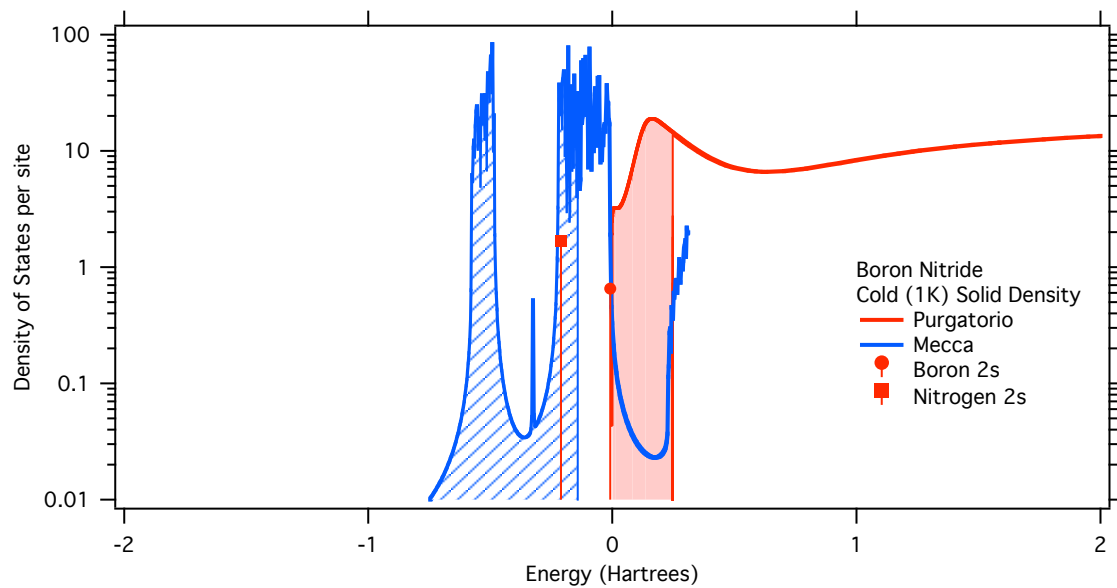
Fig[12]. Finite temperature aluminum carbide, but with the ions in their solid crystalline configuration. The shallow carbon 2S state of PURGATORIO is described by a band in MECCA. The dotted curves show the continuum density of states without the Fermi occupation factor.



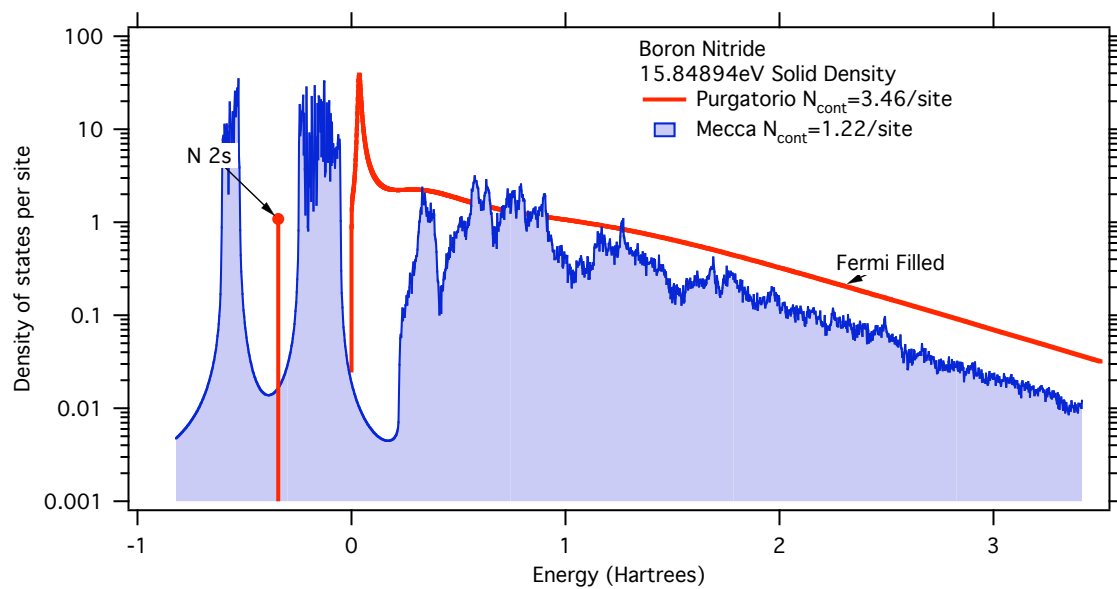
Fig[13]. An expanded view of the continuum density of states shown in the last figure, but showing ensemble snapshots of amorphous plasma ion positions. The chemical potential for the amorphous sample are in close agreement to each other and indicate adequate micro-canonical sampling.



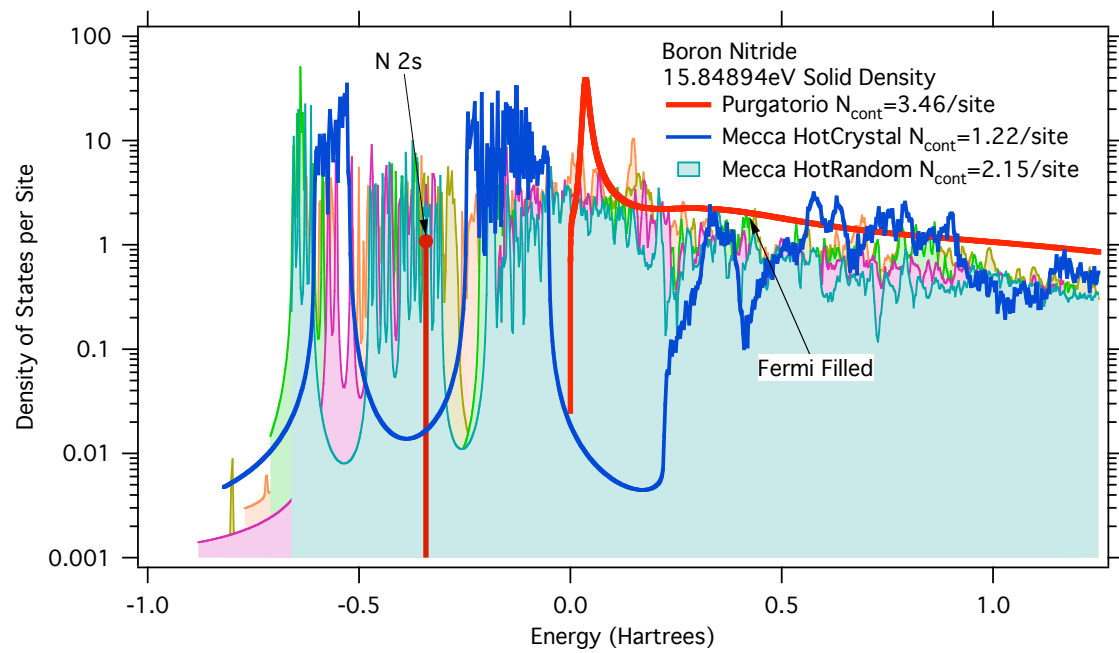
Fig[14]. Two views of the open crystal structure of Boron (red) Nitride. The size of the spheres represent the Wigner Seitz radii.



Fig[15]. Occupied density of states for cold solid Boron Nitride.



Fig[16]. The effect of heating the electrons but keeping the atoms in their crystalline order.



Fig[17]. Five representative ion position snapshots from a plasma ensemble. The average conduction electron per site is double that of the thermally excited crystal insulator, but significantly smaller than predicted by typical plasma ion-sphere models.



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